



Global Monitoring Plan on Persistent Organic Pollutants

Standard Operating Procedure for the Sampling of Water as a Core Matrix in the UNEP/GEF GMP2 Projects for the Analysis of PFOS

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Basel Convention Coordinating Centre
Stockholm Convention Regional Centre
URUGUAY



Research Centre
for Toxic Compounds
in the Environment



Standard Operating Procedure for the Sampling of Water as a Core Matrix in the UNEP/GEF GMP2 Projects for the Analysis of PFOS

Component 2 Abiotic Samples

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1 INTRODUCTION

Through decision SC-4/17 by the Conference of the Parties to the Stockholm Convention at its 4th meeting, perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F) have been listed in annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs). Subsequently, parties agreed to include water as a new core matrix for PFOS and agreed on the modalities for the sampling and analysis of PFOS. The latest version of the “Guidance on the Global Monitoring Plan for Persistent Organic Pollutants” is available as document UNEP/POPS/COP.7/INF/39.

A guidance document dedicated to the analysis of PFOS in water has been prepared by UNEP/DTIE Chemicals Branch and should be consulted for further orientation.¹ This document provides practical information as to the sampling of water for subsequent PFOS analysis in dedicated laboratories.

For orientation and further reading, reference is made to the following publication by So *et al.* ²

2 SAMPLING: CONSIDERATION OF LOCATION AND MATERIALS

For the UNEP/GEF GMP projects, active sampling has been chosen as the preferred method. This means that each sampling event will consist of a one-time grab sample by dipping a suitable container, *i.e.*, bucket, into the water and filling the sampling container.

2.1 Sampling Location and Frequency

2.1.1 Sampling Location

According to recommendations laid down in the PFOS Water guidance document ¹, the sampling location should be chosen taking into account the following characteristics:

- Mouth of a larger river or estuary;
- Easy access of the sampling site, *e.g.*, from the border of the water body, from boat, from a bridge;

2.1.2 Sampling Dates and Frequency

- At each sampling campaign, the following number of bottles will be needed:
 - Two bottles filled with water for the expert laboratory (one sample to be shipped, one sample to be stored as a retained)
 - If the country has a laboratory capable to analyse PFOS in water, a second set of two plastic bottles will be filled with water (one sample to be analysed in the local laboratory, one sample to be stored as a retained)
- Samples shall be taken at the end of each (seasonal) quarter; *i.e.*, 4 times a year on 31 March, 30 June, 30 September, and 31 December.
- If tidal water is sampled, sampling should take place at low tide to avoid the influence of marine waters. Salinity of the samples should be recorded, too.
- It is anticipated that the first sampling will be done on/around 31 December 2016.

2.2 Materials

2.2.1 General Consideration

Avoid fluorinated materials such as PTFE in materials, clothes, *etc.*

Any sampler/bucket used should be cleaned with distilled water first, then high purity methanol (LC-MS grade); dry with nitrogen/hair dryer; cover the mouth with aluminum foil and store in a PE plastic bag in the laboratory before going into the field.

The plastic bottles for sampling are 1 L in volume and can be made of HDPE or PE/PP. PE/PP bottles should be cleaned with distilled water first and then with a small volume of methanol in the laboratory; store in a PE plastic bag. Sterile HDPE bottles do not have to be cleaned before use. For this GMP2 project, MTM Research Centre will send sterile HDPE bottles.

Please note:

- To avoid cross contamination the sample bottles should only be used once.
- Take 2 samples, one for analysis and one for later confirmation if needed (retained sample).

2.2.2 Materials

Sampling equipment:

- Metal bucket (20 L/10 L)
- Clean plastic bottles, HDPE (1 L)
- Plastic bag for sampling bottle
- Plastic container for transport of bottles
- PE plastic bag for transport of bucket
- Ice (packs)
- Rope/pole



Personnel / auxiliary materials:

- Gloves
- Log book
- Water-proof pen



2.2.3 Pre-cleaning of the Sampling Bottles

Sampling will be performed using 1-L HDPE bottles. Bottles sent by MTM Research Centre are ready for use.

Preparation of sampling containers

Bottles (by MTM Research Centre)

- Plastic bottles, HDPE (1 L)
- Plastic bag
- Methanol (only in case where pre-cleaning is necessary)
- Distilled water (only in case where pre-cleaning is necessary)



Preparation of bucket (by national laboratory in the laboratory)

- 10 L/20 L metal bucket (clean)
- Wrap the mouth of the bucket with aluminium foil (see photo) and place the clean bucket into a PE plastic bag until use

Repeat this procedure before each sampling event

2.2.4 Labels

All sampling bottles and samples will be assigned a unique identifier. The letter and numbering system for the water sampling bottles is based on the labelling of the air samplers and PUFs. The same logic applies to all four UNEP/GEF GMP2 projects. A MsExcel file “GMP2_PFOs sampling and sampling codes.xlsx” is provided to assist in the work³; the narrative is below.

1. The assignment/provision of the sampling bottles (Worksheet “Overview water samples”):

| Assignment of sampling bottles for each country | | | No. analyses per year |
|---|---|--|-----------------------|
| Bottle A: | Samples 1-8 | For PFOS in expert back-up laboratory PFOS (L and br) | 4 |
| Bottle B | Samples 1-8 | For PFOS in expert back-up laboratory PFOS (L and br) | 4 |
| bottle a: | Samples 1-8 | For PFOS in national laboratory PFOS (L and br) | 4 |
| bottle b | Samples 1-8 | For PFOS in national laboratory PFOS (L and br) | 4 |
| Codes: | | | |
| Green | Analysis in expert back-up laboratory | | |
| No Fill | Analysis in national laboratory | | |
| Yellow | Groups of chemicals recommended for analysis | | |
| Bottle A/bottle a | For analysis in expert back-up/national laboratory | | |
| Bottle B/bottle b | Retained sample to be kept in the national laboratory | | |

- The sampling bottles are labelled as “Bottle ‘A’” or “Bottle ‘B’”
- Bottle ‘A’ will be shipped to the expert laboratory (after sampling)
- Bottle ‘B’ is the sample taken in parallel with Bottle ‘A’; however, the bottle will be retained in a fridge within the country
- “bottle ‘a’” and “bottle ‘b’” (note: lowercase) are the mirror samples taken in parallel with “Bottle ‘A’” and “Bottle ‘B’”; however, they will be analysed in the national laboratory (“nat’l”, if capacity exists)

This means that

- All selected countries will receive 10 bottles per year; “Bottle ‘A’” x 4 and “Bottle ‘B’” x 4 for each of the sampling events and two bottles as a field blank. Since the sampling will be for 2 years, the total number of bottles per country will be 20.

- Countries having a PFOS lab, will receive additional 10 bottles per year; "bottle 'a'" x 4 and "bottle 'b'" x 4 for mirror samples and 2 bottles for field blanks ("bottle '0'"); all for analysis of PFOS in the national laboratory. Total of 20 bottles for the 2-year period.

2. Worksheet "Georeferences"

| Country name | ISO_3 | Site/Location | Type | Latitude (deg) | Longitude (deg) | Latitude (decimal) | Longitude (decimal) |
|--------------|-------|---------------|------------------|----------------|-----------------|--------------------|---------------------|
| Egypt | EGY | | River Nile mouth | | | | |
| Vietnam | VNM | | River Mekong | | | | |

- Street address and the GPS coordinates will be recorded in a separate sheet; for reporting, we do not need this address since each country will have only one sampling site in the UNEP/GEF GMP2 project

3. Worksheet "MTM codes" - labelling of the sampling bottles for analysis in the expert laboratory

| Country (full name) | ISO_3 | Sampling Bottle | Sampling-ID | Year | Date | Season | Time code | Sampling code | Laboratory | Lab analysis code | Results code |
|---------------------|-------|-----------------|-------------|------|------------|--------|-----------|----------------|------------|----------------------|--------------|
| EGYPT | EGY | A | EGY-A | 2017 | 2017-03-31 | 1 | 2017-1 | EGY-A (2017-1) | MTM | EGY-A (2017-1) (MTM) | EGY (2017-1) |
| EGYPT | EGY | A | EGY-A | 2017 | 2017-06-30 | 2 | 2017-2 | EGY-A (2017-2) | MTM | EGY-A (2017-2) (MTM) | EGY (2017-2) |
| EGYPT | EGY | A | EGY-A | 2017 | 2017-09-30 | 3 | 2017-3 | EGY-A (2017-3) | MTM | EGY-A (2017-3) (MTM) | EGY (2017-3) |
| EGYPT | EGY | A | EGY-A | 2017 | 2017-12-31 | 4 | 2017-4 | EGY-A (2017-4) | MTM | EGY-A (2017-4) (MTM) | EGY (2017-4) |
| EGYPT | EGY | A | EGY-A | 2018 | 2018-03-31 | 1 | 2018-1 | EGY-A (2018-1) | MTM | EGY-A (2018-1) (MTM) | EGY (2018-1) |
| EGYPT | EGY | A | EGY-A | 2018 | 2018-06-30 | 2 | 2018-2 | EGY-A (2018-2) | MTM | EGY-A (2018-2) (MTM) | EGY (2018-2) |
| EGYPT | EGY | A | EGY-A | 2018 | 2018-09-30 | 3 | 2018-3 | EGY-A (2018-3) | MTM | EGY-A (2018-3) (MTM) | EGY (2018-3) |
| EGYPT | EGY | A | EGY-A | 2018 | 2018-12-31 | 4 | 2018-4 | EGY-A (2018-4) | MTM | EGY-A (2018-4) (MTM) | EGY (2018-4) |
| EGYPT | EGY | B | EGY-B | 2017 | 2017-03-31 | 1 | 2017-1 | EGY-B (2017-1) | MTM | | |
| EGYPT | EGY | B | EGY-B | 2017 | 2017-06-30 | 2 | 2017-2 | EGY-B (2017-2) | MTM | | |
| EGYPT | EGY | B | EGY-B | 2017 | 2017-09-30 | 3 | 2017-3 | EGY-B (2017-3) | MTM | | |
| EGYPT | EGY | B | EGY-B | 2017 | 2017-12-31 | 4 | 2017-4 | EGY-B (2017-4) | MTM | | |
| EGYPT | EGY | B | EGY-B | 2018 | 2018-03-31 | 1 | 2018-1 | EGY-B (2018-1) | MTM | | |
| EGYPT | EGY | B | EGY-B | 2018 | 2018-06-30 | 2 | 2018-2 | EGY-B (2018-2) | MTM | | |
| EGYPT | EGY | B | EGY-B | 2018 | 2018-09-30 | 3 | 2018-3 | EGY-B (2018-3) | MTM | | |
| EGYPT | EGY | B | EGY-B | 2018 | 2018-12-31 | 4 | 2018-4 | EGY-B (2018-4) | MTM | | |


Season codes are as follows:

| | | | | | | | | | | | |
|---|---------|--|--|--|--|--|--|--|--|--|--|
| 1 | Jan-Mar | | | | | | | | | | |
| 2 | Apr-Jun | | | | | | | | | | |
| 3 | Jul-Sep | | | | | | | | | | |
| 4 | Oct-Dec | | | | | | | | | | |

- The country is characterized by
 - Column A: Full country name
 - Column B: ISO-3 code
 - Column D: Together with the name of the sampling bottle (Bottle 'A' or Bottle 'B'); this will give the Sampling ID
- The time is coded as follows:
 - Column E: Year in Arabic numbers
 - Column F: Scheduled sampling date in format yyyy-mm-dd
 - The seasons are assigned in Roman numbers (1 – Jan to Mar; 2 – Apr to Jun; 3 – Jul to Sept; 4 – Oct to Dec)
 - Column H: Time code provides the combined information (year and season code)
 - Column L: The last column will have a condensed form the "results code" (country, year and season code)

4. As for the national samples, since they are mirror samples, same georeferences and time codes are used; however, the name of the lab is different. As an easy identifier, the full country name and the ISO-3 code are in lowercase letters (e.g., egypt and egypt); whereas for the expert labs, both are in uppercase (e.g., EGYPT and EGY).

Below is an example of a label on the sampling bottle for Egypt (Bottle A to be sent to the reference laboratory at MTM Research Centre, Örebro University)

| | |
|---|---|
|  | <p>The label is a unique identifier for the following:</p> <ul style="list-style-type: none">• Country = Egypt• Sample to be analysed in the international expert laboratory (MTM) since all letters related to the country are capitalized and bottle is 'A' (= for shipment and analysis)• Sampling date = end of season 1 in the year 2017 = 31 March 2017 |
|---|---|

2.3 Practical Arrangements for Sampling Equipment

MTM Research Centre will send pre-cleaned HDPE 1 L-bottles to the participating countries for sampling. These bottles are stored in a PE plastic bag. Please store the bottles in a clean location; it is not necessary to store the empty bottles in a fridge. As long as the bottles are not opened before the actual sampling campaign, there is no need to clean with bottles with methanol again.

Please retain the plastic bag and send it back with the filled bottle after sampling.

3 SAMPLING PROCEDURE

3.1 Sampling Location

The water samples will be taken as a grab sample during a short time within a day under the supervision of the staff assigned as “water network coordinator”. The procedure is considered “active sampling”. Guidance on the characteristics of the sampling site are provided in the PFAS guidance document [1] and include the following:

3.1.1 Geography:

- Larger (tidal) rivers (if downstream of populated area,);
- Estuary or bay;
- Tributary (before entering the main stream; please allow sufficient distance before mixture);
- Lake with a defined surrounding population;
- In all cases, make sure the water sampled is from a zone where it is mixed.

3.1.2 Further considerations for selection of sampling site:

- Ease of access from land based sites such as bridges;
- Ease of access by vessels with capacity to deploy water sampling equipment;
- Adapt the distance to shore to existing circumstances at the site.

The pictures below give examples of sampling from a boat:



3.2 Sampling

For each sampling, use the pre-cleaned bucket that is transported in a closed PE bag. To minimize contamination sources, two persons are involved in the sampling; one holding the sampling equipment and the other conducting the sampling.

Wear disposable gloves at all times.

- Upon arrival at the sampling location, remove the aluminium foil from the bucket. Rinse the bucket at least three times with sea/lake/river water from the sampling site by immersing the bucket (at least 10 cm below the surface; mark a knot on the rope); attach a weight to the bucket to help sinking;
- Fill-up the first two bottles (labelled as Bottle 'A' and Bottle 'B') with water from the bucket and discard the water from the bottles;
- Repeat once more;
- Take a fresh new water sample with the bucket and this time fill the two plastic bottles (labelled as Bottle 'A' and Bottle 'B') until the neck of the bottle (see photo below); keep these fillings as the sample, and seal the bottles carefully with the cap; put it bag in the PE plastic bag;
- Store the bottles in the plastic container and place the ice packs. Close the container until arrival at the laboratory;
- Repeat the above steps if samples are needed for the national laboratory (labelled as bottle 'a' and bottle 'b').
- After sampling, store the bucket in the PE bag it came in;
- Please record additional parameters such as in relation to location, sampling personnel, *etc.*

Once a year, collect a field blank, which will be an empty bottle labelled 'O'. Please note that the field blank bottle will not be rinsed with water and filled with water. The field blank is collected as follows: Take one empty pre-cleaned bottle together with Bottle 'A' and Bottle 'B' and open all lids at the same time. Keep it open during the sampling activity and then close it at the same time the Bottle 'A' and Bottle 'B' are closed. Put the label on the field blank. Then place the field blank together with the samples A and B.

Take pictures of each sampling event and send to MTM Research Centre.

3.3 Storage, packaging and shipment

Store all bottles cold, but not frozen, in a fridge (+4 °C). Ensure that it is closed well; possibly add extra plastic wrapping. Keep the samples cold during shipment with ice-packs. If sending the samples by courier; notify the contact person in advance and supply us with the courier name and tracking number after dispatch.

The shipment modalities shall be agreed in close cooperation between the country and the international expert laboratory. The frequency will depend on storage conditions. The preferred option is to ship the water sample as soon as possible, *i.e.*, in the week after the sampling. Please use the polystyrene boxes provided. In addition, consult with the workplan of your national/regional project. It is recommended to ship the water samples together with the air samples (PUFs from samplers 5 and 11) that are handled by MTM Research Centre, Örebro University.

4 DOCUMENTATION

A MsExcel file is provided to document each sampling event. The MsExcel file contains the following worksheets and information:

1. Worksheet “Georeferences”

This worksheet provides a summary of all information related to the location and conditions where the sampling takes place:

| | |
|--------------------------|---|
| Country name: | Full name and ISO_3 code |
| Site/Location: | Short name assigned (preferably containing name of the water body) |
| Address: | Physical address |
| Type of water | Fresh, marine, brackish |
| GPS coordinates: | degrees: Latitude and longitude decimals: Latitude and longitude |
| Narrative: | Brief narrative description of location (such as outside of harbour, downstream city) |
| Distance from shore: | in meter (m) |
| Sampling procedure: | Briefly describe: from shore, from bridge, by boat, <i>etc.</i> |
| Institution responsible: | Please provide name of institution undertaking the water sampling. |
| Photo: | please insert a photo of the sampling site |

2. Worksheet “MTM Bottles”

The screenshot of this worksheet is shown below. Please fill in the cells according to the actual sampling situation. It is anticipated that the bottles ‘A’ and ‘B’ and the bottles ‘a’ and ‘b’, where applicable, will be taken at the same time, by the same persons, at same weather and other conditions. Therefore, the worksheet “nat’l bottles” is a copy of the worksheet “MTM Bottles” applying the rationale as described in section 2.2.4 - Labels, *i.e.*, lowercase letters for the samples targeted for

analysis in the national laboratory. However, storage location or shipment of samples for analysis may differ between these two and between sampling events.

This electronic logbook is designed for the "water network coordinator" to assist and document the field work under the UNEP/GEF GMP2 projects. These worksheets are closely interlinked with the MsExcel file "GMP2_PFOS sampling and sample codes".

Please note the following:

- The worksheets "MTM Bottles" and "nat'l bottles" shall be filled out after each sampling event
- Please fill in the actual data (date, time, personnel, etc.);
- Note any deviation from scheduled procedure in a new column named "Comments";
- Please use date (dd-mmm-yyyy) and time (hh:mm) formats according to the cell format.

| 1 | A | B | C | D | E | F | G | H | I | J | K | L | M | N |
|----|----------------|------------------|--|--------|---------------------|------------------------|--|---|---------------|--------------|------------|--|--------------------|-----------------------------|
| | Sampling code | Site/Location | GPS coordinates of site (latitude/longitude) | Bottle | Weather observation | Water temperature (C) | Name of persons who undertook sampling | | Sampling date | Time - from: | Time - to: | Place where sample stored until analysis | Storage conditions | Shipment date to laboratory |
| 2 | EGY-A (2016-4) | River Nile mouth | link to "by country" | A | cloudy, no rain | | | | 31-Dec-2016 | 13:00 | 14:30 | | | |
| 3 | EGY-B (2016-4) | River Nile mouth | link to "by country" | B | | | | | | | | | | |
| 4 | EGY-A (2017-1) | River Nile mouth | | A | | | | | 31-Mar-2017 | | | | | |
| 5 | EGY-B (2017-1) | River Nile mouth | | B | | | | | | | | | | |
| 6 | EGY-A (2017-2) | River Nile mouth | | A | | | | | 30-Jun-2017 | | | | | |
| 7 | EGY-B (2017-2) | River Nile mouth | | B | | | | | | | | | | |
| 8 | EGY-A (2017-3) | River Nile mouth | | A | | | | | 30-Sep-2017 | | | | | |
| 9 | EGY-B (2017-3) | River Nile mouth | | B | | | | | | | | | | |
| 10 | EGY-A (2017-4) | River Nile mouth | | A | | | | | 31-Dec-2017 | | | | | |
| 11 | EGY-B (2017-4) | River Nile mouth | | B | | | | | | | | | | |
| 12 | EGY-A (2018-1) | River Nile mouth | | A | | | | | 31-Mar-2018 | | | | | |
| 13 | EGY-B (2018-1) | River Nile mouth | | B | | | | | | | | | | |
| 14 | EGY-A (2018-2) | River Nile mouth | | A | | | | | 30-Jun-2018 | | | | | |
| 15 | EGY-B (2018-2) | River Nile mouth | | B | | | | | | | | | | |
| 16 | EGY-A (2018-3) | River Nile mouth | | A | | | | | 30-Sep-2018 | | | | | |
| 17 | EGY-B (2018-3) | River Nile mouth | | B | | | | | | | | | | |
| 18 | | | | | | | | | | | | | | |
| 19 | | | | | | | | | | | | | | |
| 20 | | | | | | | | | | | | | | |
| 21 | | | | | | | | | | | | | | |
| 22 | | | | | | | | | | | | | | |
| 23 | | | | | | | | | | | | | | |
| 24 | | | | | | | | | | | | | | |

5 CONTACT INFORMATION

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6 ABBREVIATIONS

| | |
|--------|---|
| GEF | Global Environment Facility |
| GMP | global monitoring plan (under the Stockholm Convention on POPs) |
| HDPE | high-density polyethylene |
| L | litre |
| PE | polyethylene |
| PFOS | perfluorooctane sulfonic acid |
| PFOS-F | perfluorooctane sulfonyl fluoride |
| POPs | persistent organic pollutants |
| PP | polypropylene |
| PTFE | polytetrafluoroethylene (Teflon) |
| UNEP | United Nations Environment Programme |

7 REFERENCES

- ¹ UNEP (2015): Guidance on PFAS analysis in water for the Global Monitoring Plan on POPs. <http://www.unep.org/chemicalsandwaste/Portals/9/POPs/PFAS/Guide%20PFAS%20waterUNEP%202015.pdf>
- ² M.K. So, S. Taniyasu, N. Yamashita, J.P. Giesy, J. Zheng, Z. Fang, S.H. Im, and P.K.S. Lam (2004): Perfluorinated Compounds in Coastal Waters of Hong Kong, South China, and Korea. *Environ. Sci. Technol.* **38**, 4056–4063
- ³ For download from [www.unep.org/chemicalsandwaste/...](http://www.unep.org/chemicalsandwaste/)